

University contributions and collaborations in CalNex

*CalNex Science Team Meeting
16 May 2011, Sacramento, CA*

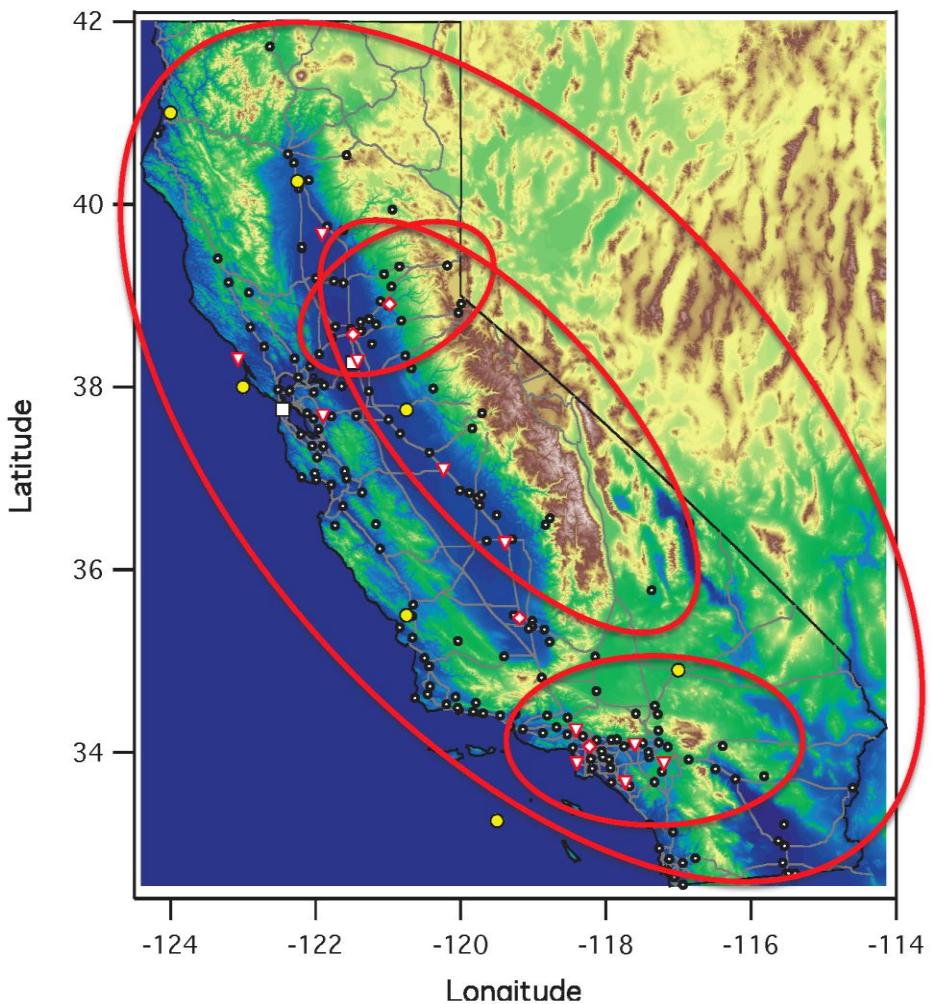
Presented by:
Steven C. Wofsy
Harvard University

CalNex 2010

Measurements during CalNex:

- Long-term surface observations
- Instrumented tall towers
- Major intensive ground sites
- Daily ozonesonde launches
- Mobile research platforms
 - NOAA WP-3D & Twin Otter
 - CIRPAS Twin Otter
 - NASA King Air
 - DOE G-1
 - R/V *Atlantis*
- Satellite observations
 - TES, OMI, Sciamachy, IASI

CalNex and CARES aircraft operations



University researchers and supporting agencies:

NOAA P-3 (*research groups...*):

Wofsy (Harvard), Atlas (Miami), Blake (Irvine), Nenes (Georgia Tech), Pilewskie (U. Colorado)—(funded by NOAA CPO, NSF, NASA, and CARB)

CIRPAS Twin Otter:

Prather and Seinfeld groups (Cal Tech, funded by NOAA CPO and CARB)

IONS ozonesondes: Supported by NOAA, NASA, US Navy, Environment Canada; National Park Service, CA State Parks, Naval Postgraduate School, and the FAA

WGC tower: Fischer (Berkeley, LBL) and Andrews (Cal Energy Comm & NOAA)

R/V Atlantis: Bertram, Crisp: UCSD (NSF); Cassandra Gaston: UCSD (NOAA CPO); Frossard: UCSD (NSF); Brian Heikes: U. Rhode Island (NOAA CPO); Bill Keene, John Maben: Univ. Virginia (NSF); Ibraheem Nuaaman, Alexander Vlasenko: York University, Canada (Environment Canada); Chris Cappa, Dan Mellon: UC Davis (NOAA CPO); Theran Riedel: Univ Washington (NSF); Joanna Kinsey: SUNY (NSF); Byron Blomquist: Univ Hawaii (NOAA)

More: Bakersfield; CARES; CalMEX; LA-Urban (Cal Tech) following...

Bakersfield CalNex2010 Team

Major Funding Cal ARB

Gas measurements

Brune (Penn State)

Cohen (UCB)

Goldstein (UCB)

Goldstein/Baer (UCB/LGR)

Keutsch (UWi)

Murphy (U Toronto)

Ren (U Miami)

Thornton (UWa)

Wennberg (CalTech)

Wilczak (NOAA)

Zondlo (Princeton)



OH, HO₂, OH reactivity

NO, NO₂, peroxy nitrates, RONO₂, HNO₃

VOCs, CO, O₃, Met

CO, N₂O, CH₄, H₂O, CO₂

H₂CO, HCOHCO, α -dicarbonyls

IC and IR, water soluble gases

HONO, Met

PAN, PPN, MPAN, RO₂NO₂, etc.

H₂O₂, CH₃OOH, HNO₃, HO₂NO₂, HCN, etc.

Boundary Layer, Met

NH₃

Particulate measurements

ARB

Brune (Penn State)

Cohen (UCB)

Glasius (U Aarhus, DK)

Goldstein (UCB)/Hering (ADI)

Murphy (U Toronto)

Offenberg (EPA)/Surratt (UNC)

Russell (UCSD)

OC/EC

Potential aerosol mass

Particle organic nitrates

Organonitrates, organosulfates (filters)

TAG speciated organics, MOUDI samples

IC and IR, water soluble particles

Aerosol Composition (filters)

AMS, FTIR, SPMS, trace elements

CalNEX Los Angeles



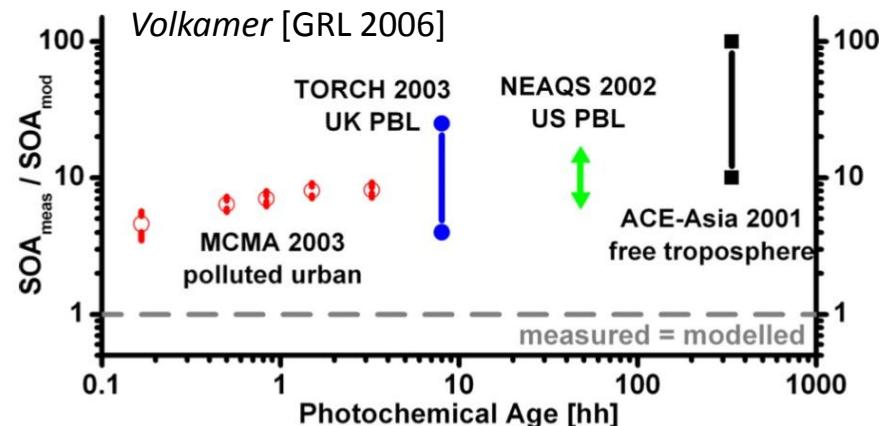
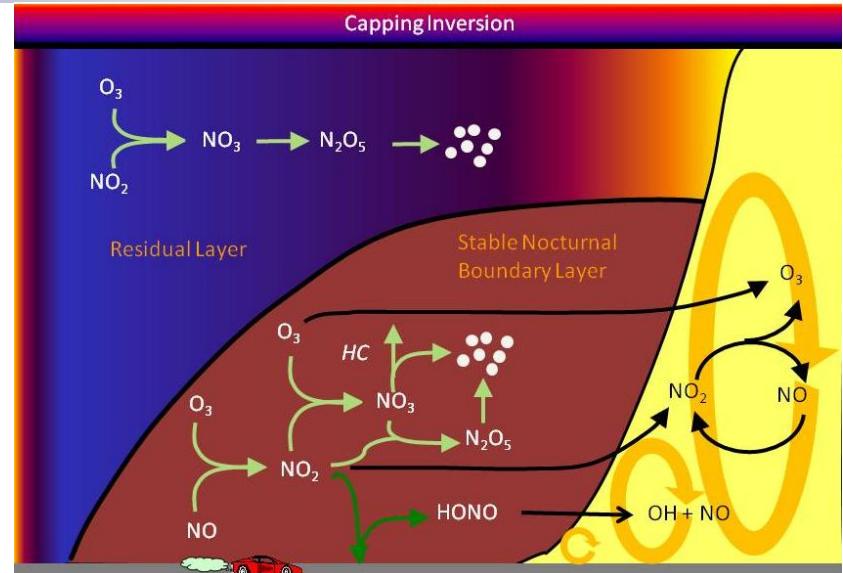
Aerosol Dynamics
Aerodyne Research
Arizona State University
Baylor University
Brookhaven National Laboratory
California Air Resources Board
California Institute of Technology
Carnegie Mellon University
Consejo Superior de Investigaciones
Cientificas
Droplet Measurement Technologies
Georgia Institute of Technology
Indiana University
Istituto di Scienze dell'Atmosfera e
del Clima

Jet Propulsion Laboratory
Laboratoire Inter-Universitaire des
Systemes Atmospheriques
Loyola Marymount University
Massachusetts Institute of Technology
Max Planck Institut fur Chemie
NOAA Air Resources Laboratory
NOAA Earth System Research Laboratory
Pacific Northwest National Laboratory
Paul Scherrer Institut
Texas Tech University
Tofwerk AG
US Environmental Protection Agency
USFS Fire Sciences Laboratory
University of Calgary
University of California-Berkeley

University of California-Berkeley
University of California-Davis
University of California-Irvine
University of California-Los Angeles
University of California-San Diego
University of Colorado-Boulder
University of Delaware
University of Houston
University of Manchester
University of North Carolina-Chapel Hill
Universite Saint-Joseph de Beyrouth
University of Toronto
University of Utrecht
University of Washington-Seattle
University of York

Motivation

- Ozone formation in Los Angeles
- Radical Chemistry / Budget
- Nocturnal Chemistry and Mixing
- Chlorine chemistry
- NO_y budget

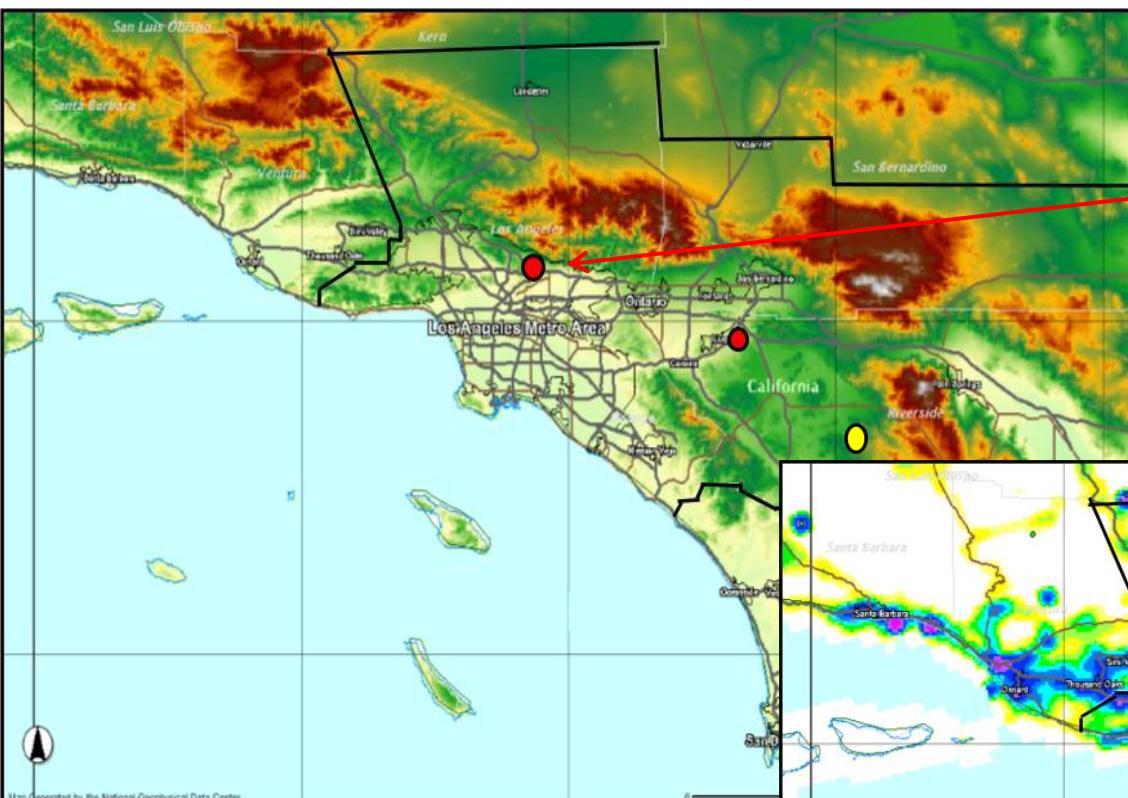


SOA formation with anthropogenic VOCs > biogenic VOCs

- OA characterization by most comprehensive suite of instruments
- Emissions and chemistry of semi-volatile organic compounds (SVOCs)
- Aqueous-phase chemistry

CalNex-Los Angeles Site

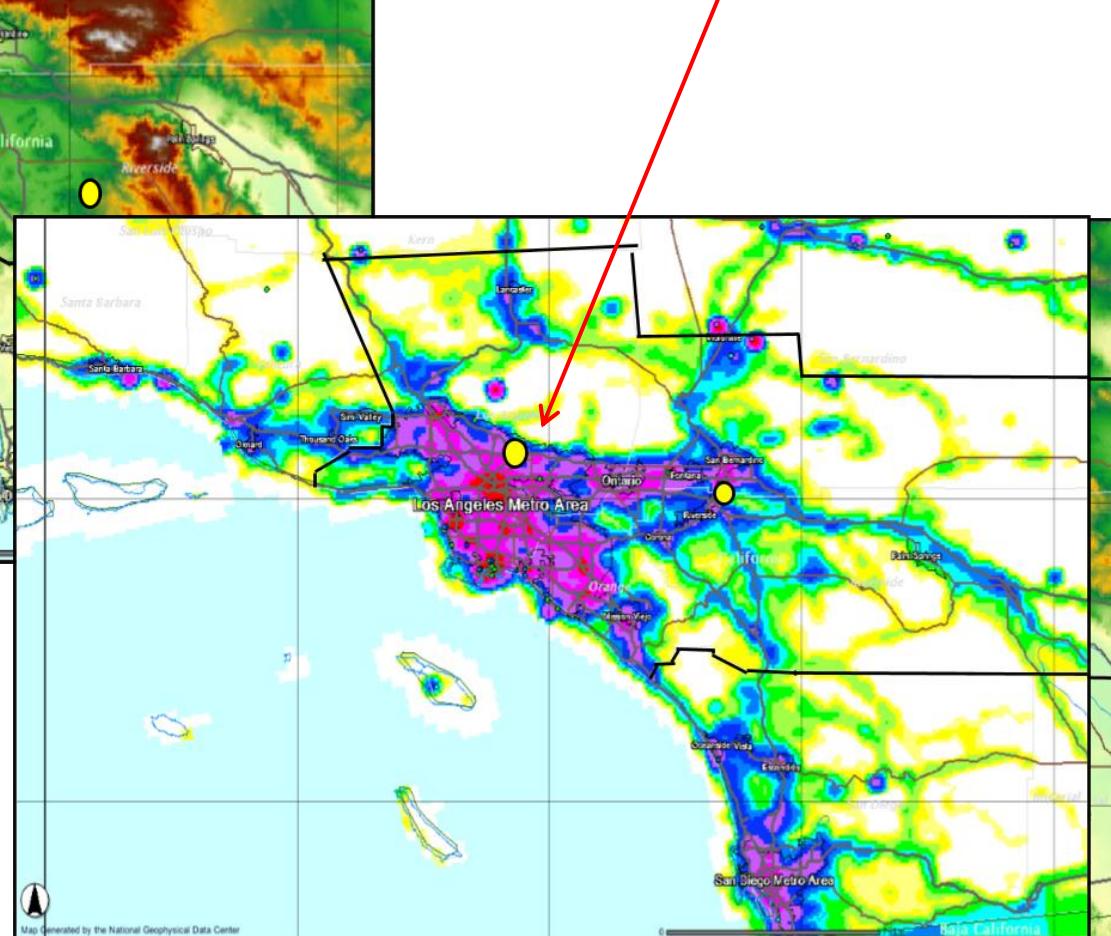
CANEX
LOS ANGELES



Caltech

Topography

Total pollutant emissions



NOAA National Emission Inventory
(<http://map.ngdc.noaa.gov/website/al/emissions/viewer.htm>)

Field Setup at Caltech

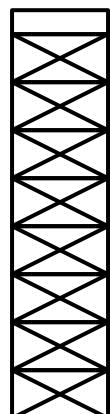
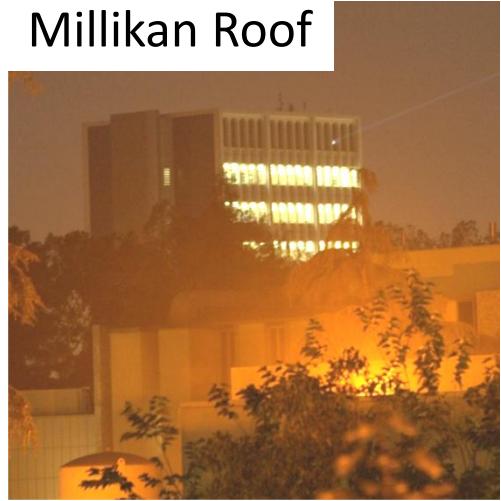
Main Site



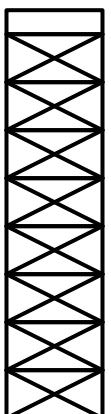
Keck Roof



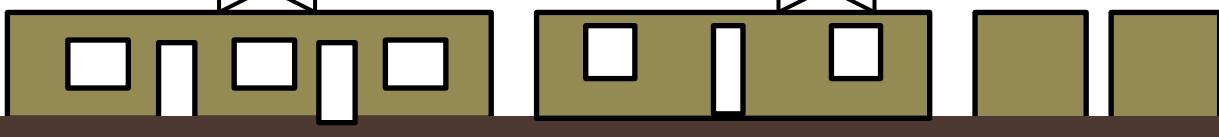
Millikan Roof



Aerosol and Gas
sampling towers
10m high



9 Lab Trailers (2000 sq²)
70 instr. / 16 samplers
2000 amp power
50 – 70 participants



Gas-Phase Measurements

VOCs	GC-MS, online VOCs	NOAA
O ₃ , NO ₂ , SO ₂ , NO ₃ , HONO, HCHO	DOAS	UCLA
OH and HO ₂ , OH reactivity	LIF – FAGE	Indiana Univ.
Photolysis frequencies, Total sky imager	Scanning Actinic Flux Spectroradiometer	Univ. of Houston
O ₃ , SO ₂ , NO/NO _x , NO _y , CO	UV Abs / Flour/ CL+ photolysis cell and Mo converter / VUV	Univ. of Houston
Organic acids, HONO, HNCO, HCl , HNO ₃	CIMS	NOAA
HCHO	Hantzsch reaction fluorescence	Univ. of Houston
CHOCHO, HONO, NO ₂	CEAS	NOAA
PANs	GC-ECD	NOAA
CINO ₂ , PANs	CIMS	U. Calgary
CO / CO ₂	VUV / NDIR absorption	NOAA
gas phase and semivolatile organics	High-resolution PTR-TOF MS	U. Utrecht
water-soluble OC in the gas-phase	PILS and mist chamber + online WSOC	Georgia Tech
total gas-phase organics, & semivolatiles	High Resolution EI-TOF-MS	MIT
gas-phase semivolatiles	Sorbent tubes + off-line TD-GCMS	CMU
urban meteorology, eddy covariance	various	NOAA ARL
HCHO, CHOCHO, NO ₂ , aerosol SCD	MAX-DOAS	CU Boulder
NH ₃	QC-TILDAS	Univ. of Toronto
Soluble gases (HNO ₃ , NH ₃)	GP-IC	CARB
13CO ₂	WS-CRDS	Caltech
Organic acids + other organics	MOVI-TOF-CIMS	Univ. of Washington
Daily canister for VOC analysis	Offline GC- FID / MS	US EPA Research
CHOCHO, NO ₂	LED-CE-DOAS	CU Boulder
Met parameters	Ground site Caltech Library Roof	NOAA / Caltech
HONO	Wet Chemical (HPLC)	
semivolatile gas-phase hydrocarbons	solid adsorption and liquid extraction	Loyola Marymount

Aerosol Measurements

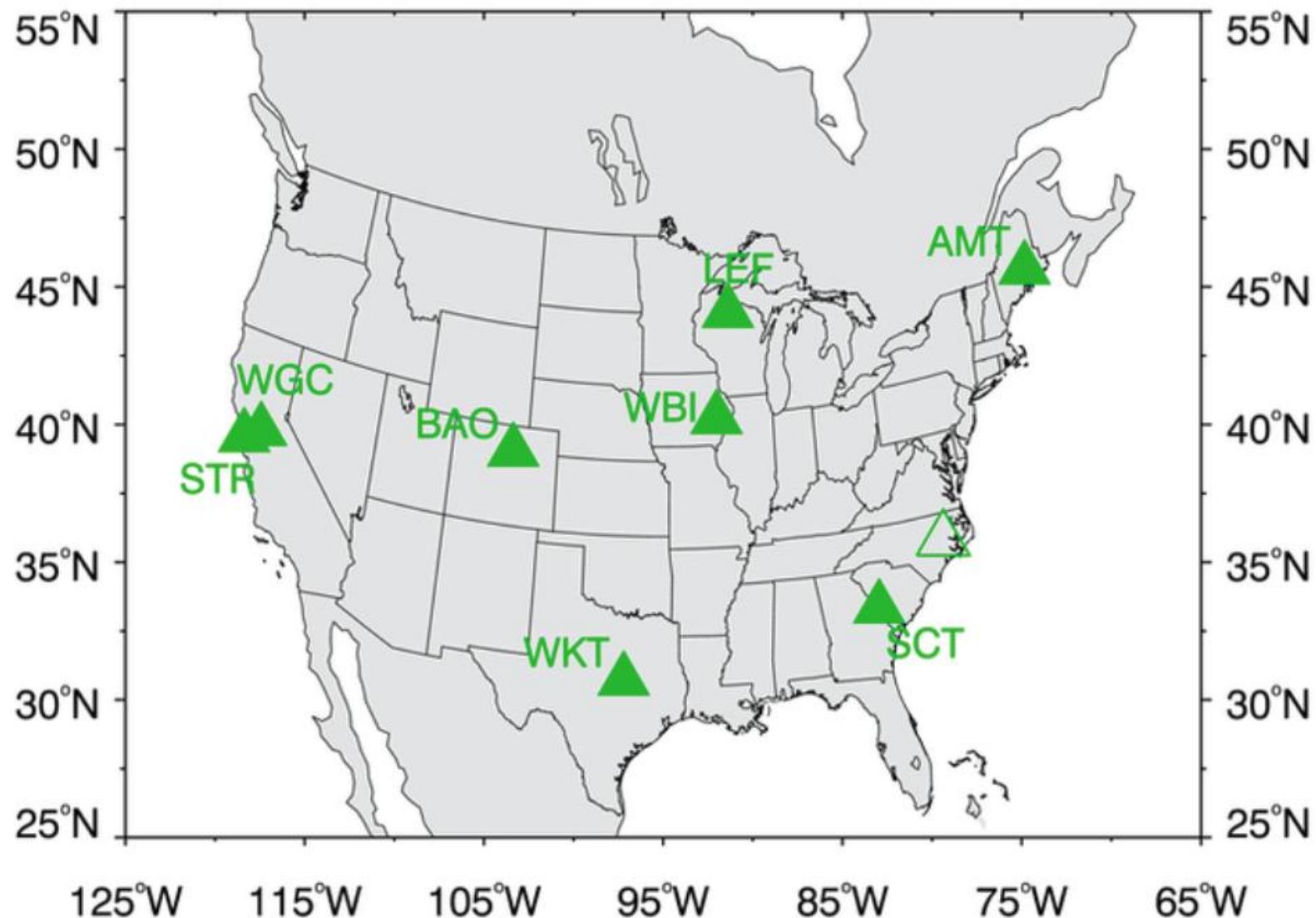
Size resolved submicron chemical comp.	High-resolution ToF-AMS (HR-ToF-AMS)	CU Boulder
Potential aerosol mass	PAM	U-Boulder & Penn State
Organic aerosol composition	Soft-Ionization HR-ToF-AMS	CU Boulder
Submicron particle number distributions	TSI SMPS	CU Boulder
SO ₄	Research-quality monitor	CARB
Total particle number	TSI Water CPC 3786	CU Boulder
Particle number distrib.(300 nm - 10 um)	Grimm OPC 1.109	CU Boulder
OC and EC	1 hr Sunset Labs thermal-optical analyzer	Georgia Tech
water-soluble OC in Particles	PILS and mist chamber + online WSOC	Georgia Tech
PM2.5 carboxylic acids	PILS + ion chromatography and CIMS	Georgia Tech
1-hr molecular tracers (particles and semivol.)	TAG-AMS	UC Berkeley, Aer. Dynamics, Aerodyne, CU-Boulder)
1-hr molecular tracers (part. & semivol.)	2-D Thermal-Desorption Aerosol GC-MS (TAG)	UC Berkeley, Aer. Dynamics
PM semivolatile and non-volatile organics	High-resolution PTR-TOF MS	U. Utrecht
HR-MS analysis of WSOC/N compounds	PILS-collector + Electrospray-Orbitrap UHR MS	DOE PNNL EMSL
Black carbon & coating Composition	SP-AMS	U. Manchester, UK
Black carbon	7-Wavelength Aethalometer	U. Manchester, UK
Black carbon absorption	DMT 3-Wavelength Photoacoustic Sensor	U. Manchester, UK
Black carbon mass	DMT SP2 (Soot Particle Soot Photometer)	U. Manchester, UK
Single particle composition 200-5000nm	PALMS	NOAA
Single nanoparticle composition	NAMS	U. Delaware
Cloud condensation nuclei (CCN) spectrum	DMT CCN Counter	Brookhaven NL
Size-resolved CCN	SMPS + DMT CCN	Brookhaven NL
Ions in aerosol (SO ₄ , NO ₃ , Cl, K, etc.)	GP-IC	CARB
Particle-phase organic acids + other organics	MOVI-TOF-CIMS	Univ. of Washington
Submicron particle number distributions	TSI SMPS #2	CU Boulder
Submicron size distribution	UHSAS	CU Boulder
Supermicron size distribution & PBAP	UV-APS	CU Boulder

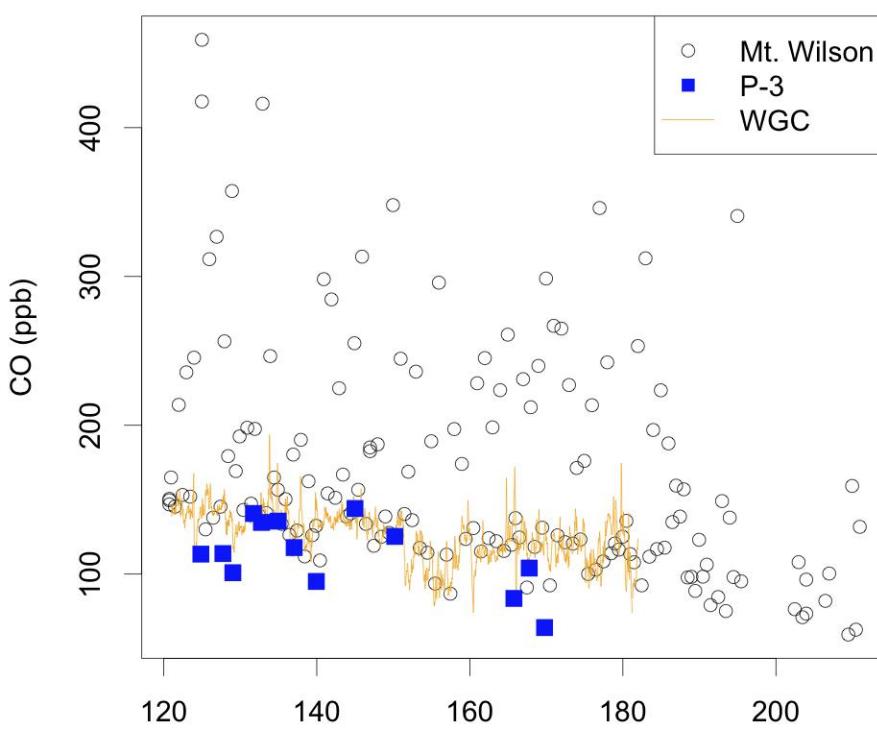
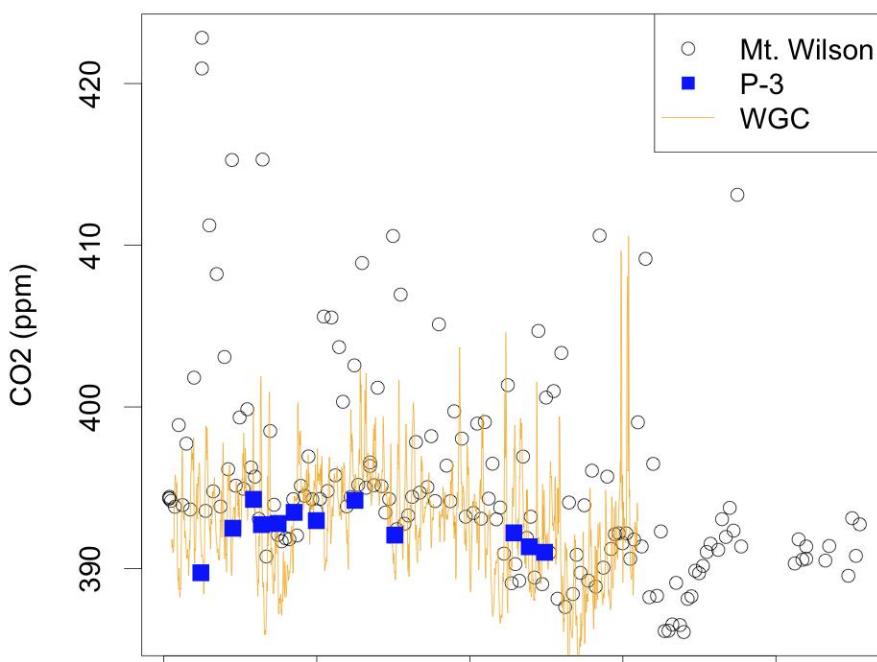
Aerosol Measurements (cont.) + Samplers

particle extinction 532 nm	Cavity attenuated phase shift (CAPS)	Aerodyne
particle extinction 630 nm	CAPS	Aerodyne
single-particle single scattering albedo	ASTER	NOAA
aerosol LIDAR	3-wavelength LIDAR	USFS
Column aerosol optical depth	Sunphotometry / AERONET Station	UCLA
Aerosol extinction, scattering, albedo	CRDS / integrating sphere nephelometry	TTU
Boundary layer backscatter & height	Vaisala Ceilometer	Univ. Houston / UCLA

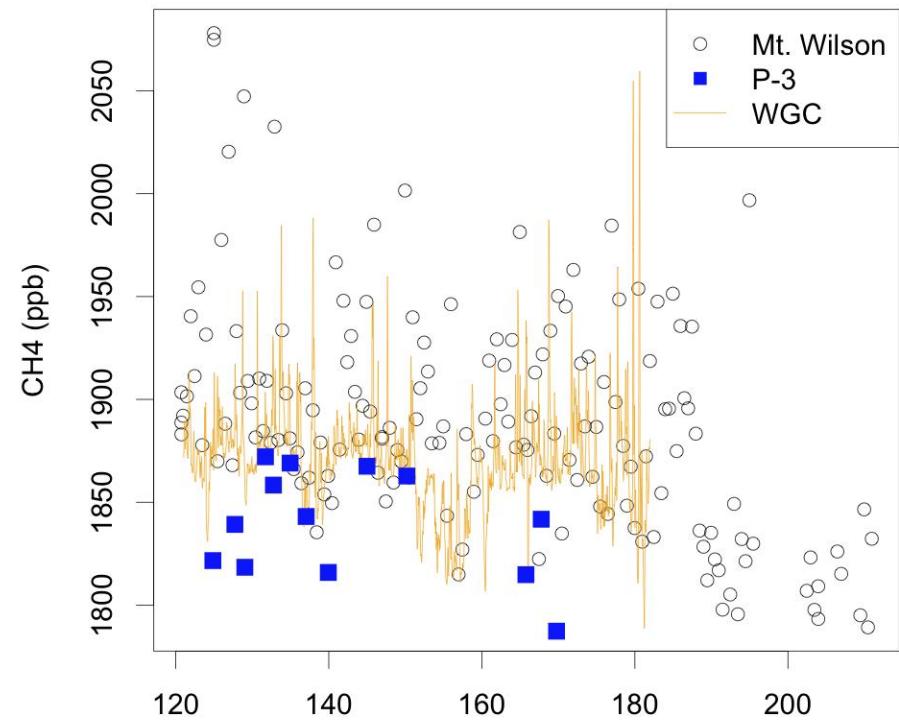
NMR analysis of WSOC	CNR-ISAC, Italy
Organosulfates and nitrooxy organosulfates	Caltech/UNC
OOA characterization	University of York, UK)\
14C analysis of OC, EC, Water-Insoluble OC (WIOC) and WSOC (24 hr)	PSI, Switzerland
14C analysis of Total Carbon (~3 hr for 100 samples)	PSI, Switzerland
Elements and metals (2-hr resolution)	PSI, Switzerland
HR-MS analysis of organic compounds	DOE PNNL EMSL
Precursor-specific SOA Tracers	US EPA Research
Compound-Specific Stable Isotope Analysis for SOA characterization and evolution	Baylor Univ.
14C analysis of Total Carbon	US EPA Research
Molecular speciation of OA	CSIC, Spain
size resolved elements and mass in 8 sizes < PM10	UC Davis
modified FRM - PM2.5 mass	US EPA Research)\
Microanalysis Particle Samplers	ASU
Functional Group Contributions and potentially PMF	UCSD
Sample Archiving for future analyses	Georgia Tech
Filter Sampler	CMU
Sorbent Sampler	CMU
Derivatization and direct thermal desorption with analysis by GCxGC-TOFMS	UC Berkeley
Metals and trace elements	CSIC

Walnut Grove Tall Tower

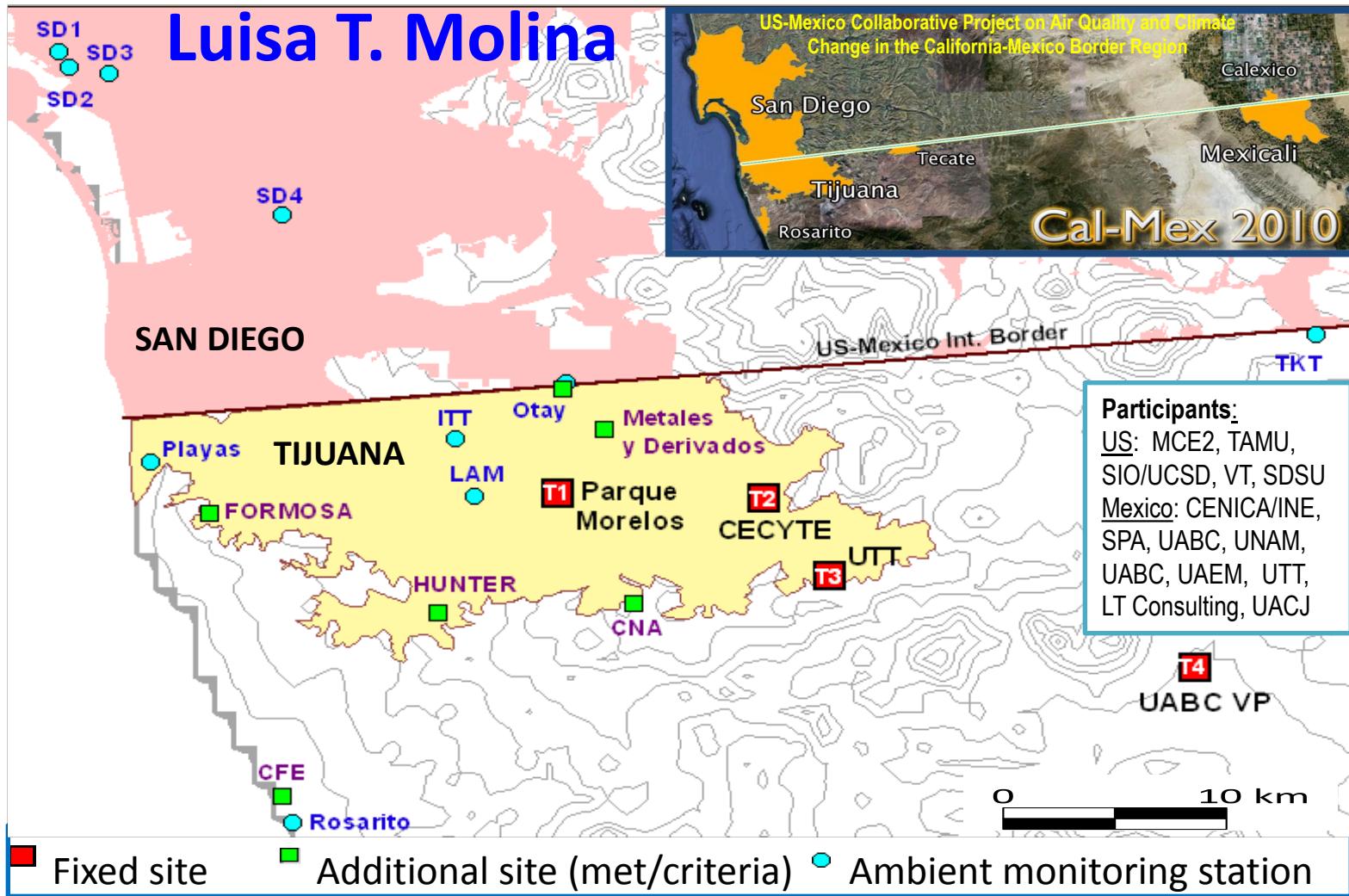




Mt. Wilson and WGC: Putting the CalNEX measurements in context, spatially and temporally



Monitoring sites during Cal-Mex 2010



Central fixed site: Parque Morelos; 4 sites for criteria pollutants & meteorology;

2 Meteorological stations; Various sites for sampling of VOCs, PM and others;

Mobile laboratory from VT and Mini-DOAS from MCE2 circulated in various locations

Black Carbon Measurements during Cal-Mex 2010

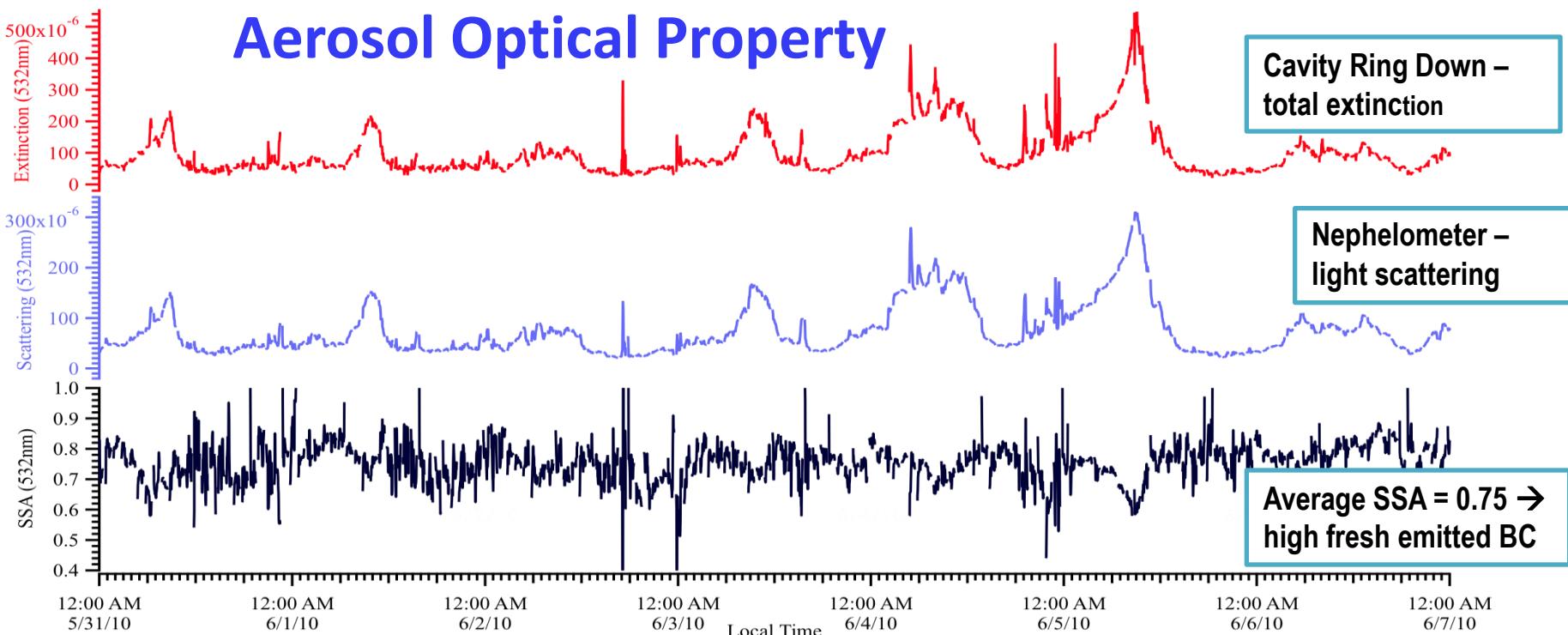
Black Carbon (BC): Harmful air pollutant that has substantial regional and global climate impacts. BC are particles resulting from the incomplete combustion of fossil fuels, wood and other biomass.

BC instruments: Aethalometers , PSAP, Cavity ring-down, SP2, OC/EC (deployed at various sites on both sides of the border)

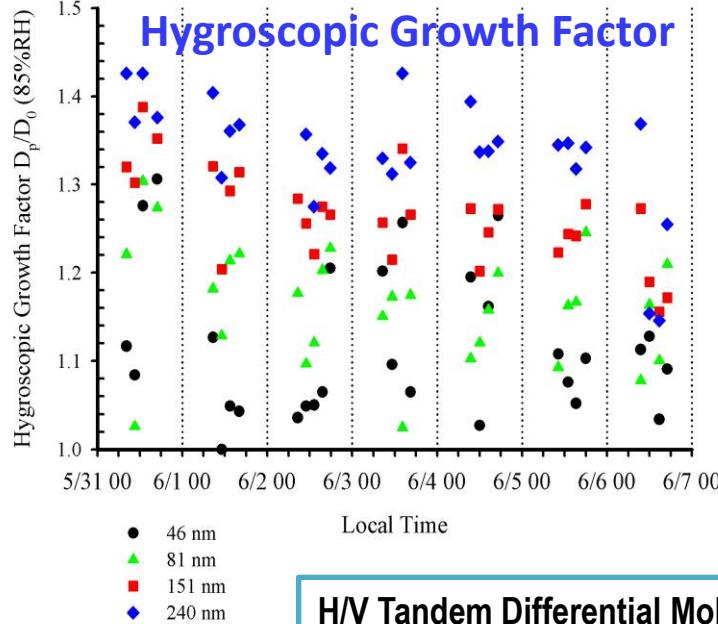
Preliminary Results:

- High concentrations of BC were observed in Tijuana
 - daily average range: 1-7 $\mu\text{g}/\text{m}^3$ with marked diurnal patterns;
 - compared with ~ 2 - 4 $\mu\text{g}/\text{m}^3$ in Mexico City and the surrounding region during MILAGRO in 2006.
- Observed recurrent nighttime high BC episodes.
- Found association of BC with organic mass fragments, PAHs, CO, NOx, optical properties and particle size.
- Correlation with organic aerosol markers and components suggesting that elevated concentrations observed were attributed to vehicular emissions (weekday mornings) and burning activities (weekend evenings).

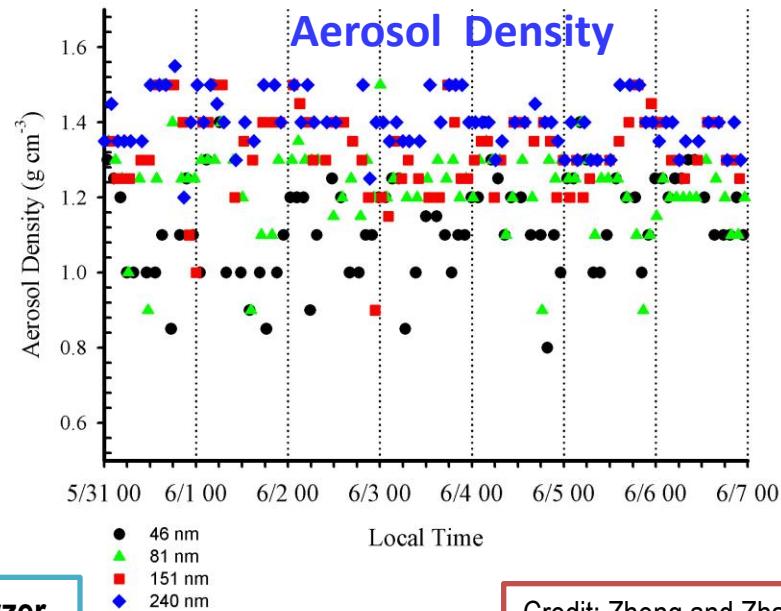
Aerosol Optical Property



Hygroscopic Growth Factor



Aerosol Density



H/V Tandem Differential Mobility Analyzer

Cavity Ring Down –
total extinction

Nephelometer –
light scattering

Average SSA = 0.75 →
high fresh emitted BC

Credit: Zheng and Zhang (TAMU)

CALNEX Maersk Encounter P-3, Atlantic

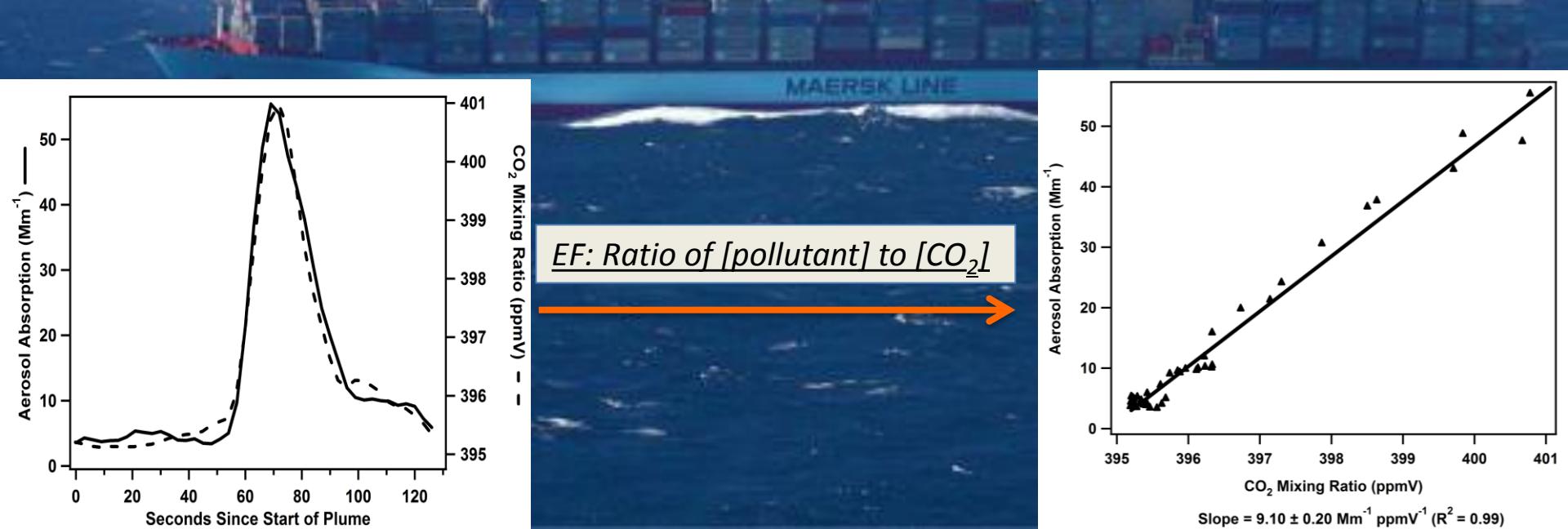
California (future US/global) law: vessels switch from Hi to Lo Sulfur Fuel

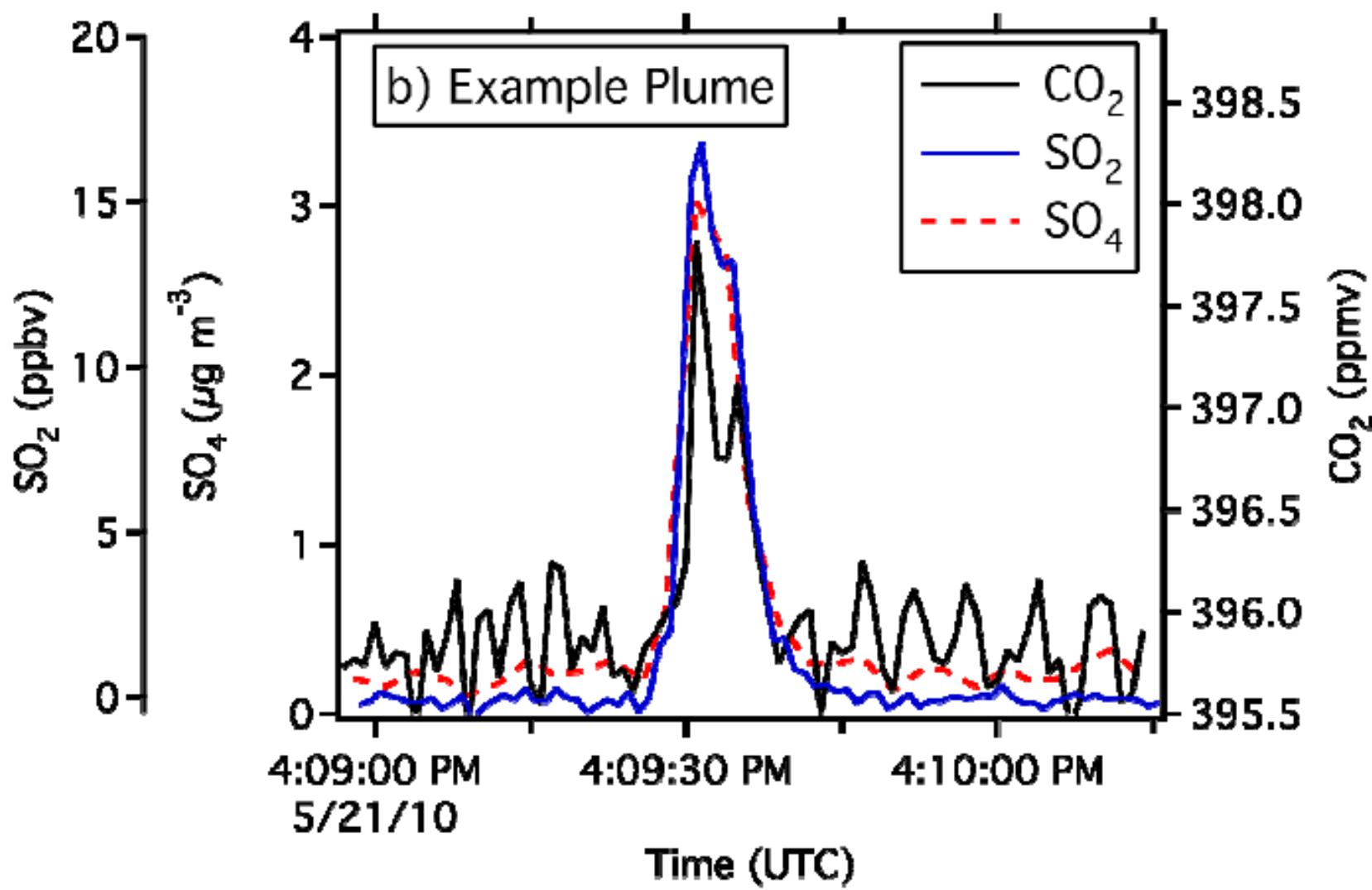
CALNEX: Emissions (EF – g / kg fuel) measured as vessel changed from Hi to Lo

Research Aircraft and Ship: Measured SO₂, Sulfate, Organic Matter, Black

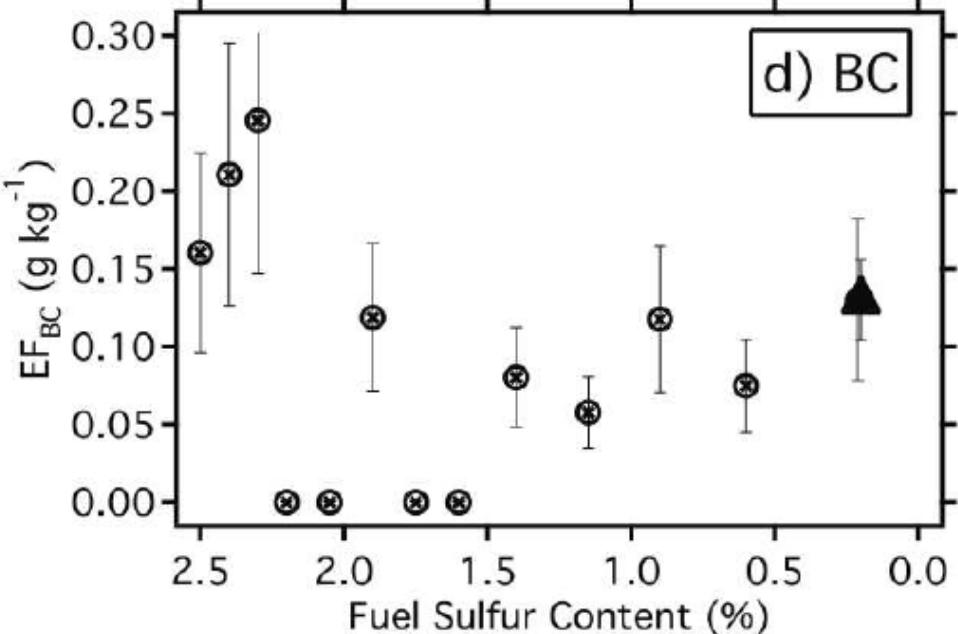
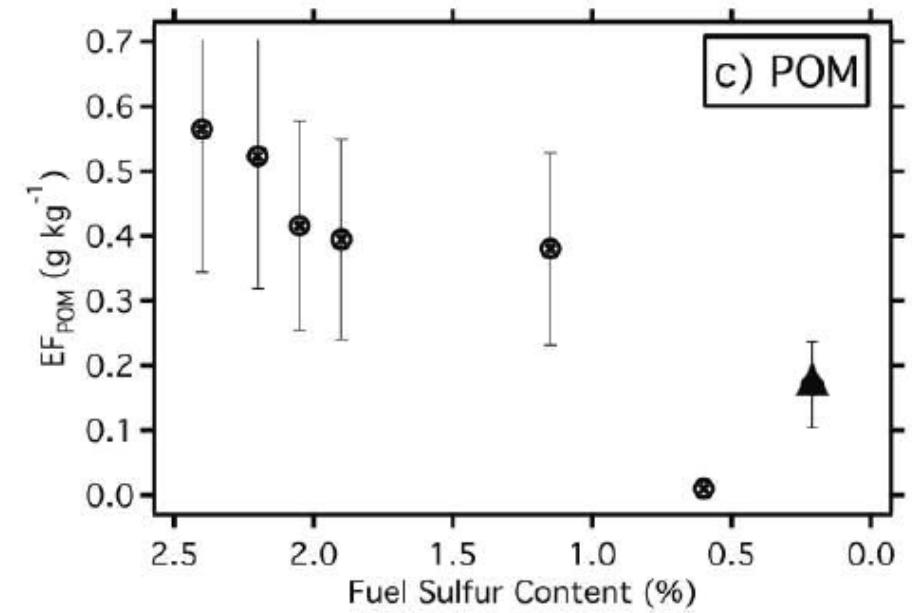
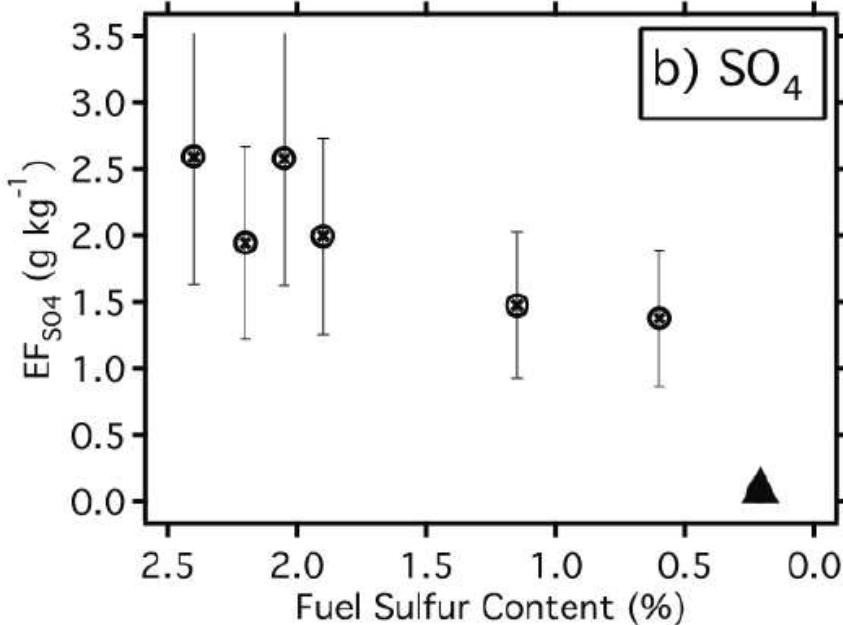
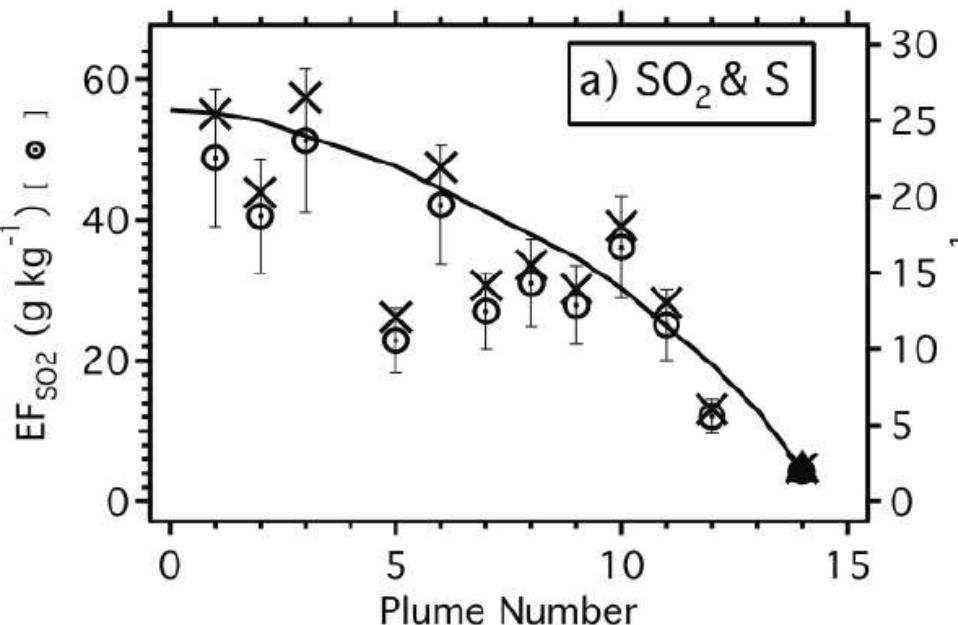
CO₂: Essential to EF calculations. Used to relate [pollutant] to fuel consumed

Lack, D., C. Cappa, J. Langridge, R. Bahreini, G. Buffaloe, C. A. Brock, K. Cerully, K. Hayden, J. Holloway, B. Lerner, S.-M. Li, P. Massoli, R. McLaren, A. M. Middlebrook, R. H. Moore, A. Nenes, I. Nuaaman, T. Onasch, J. Peischl, A. Perring, P. K. Quinn, T. B. Ryerson, J. P. Schwarz, J. R. Spackman, Steven C. Wofsy, D. Worsnop, Bin Xiang and E. Williams (2011). "Impact of Fuel Quality Regulation and Speed Reductions on Shipping Emissions: Implications for Climate and Air Quality." Submitted to Environmental Science and Technology.

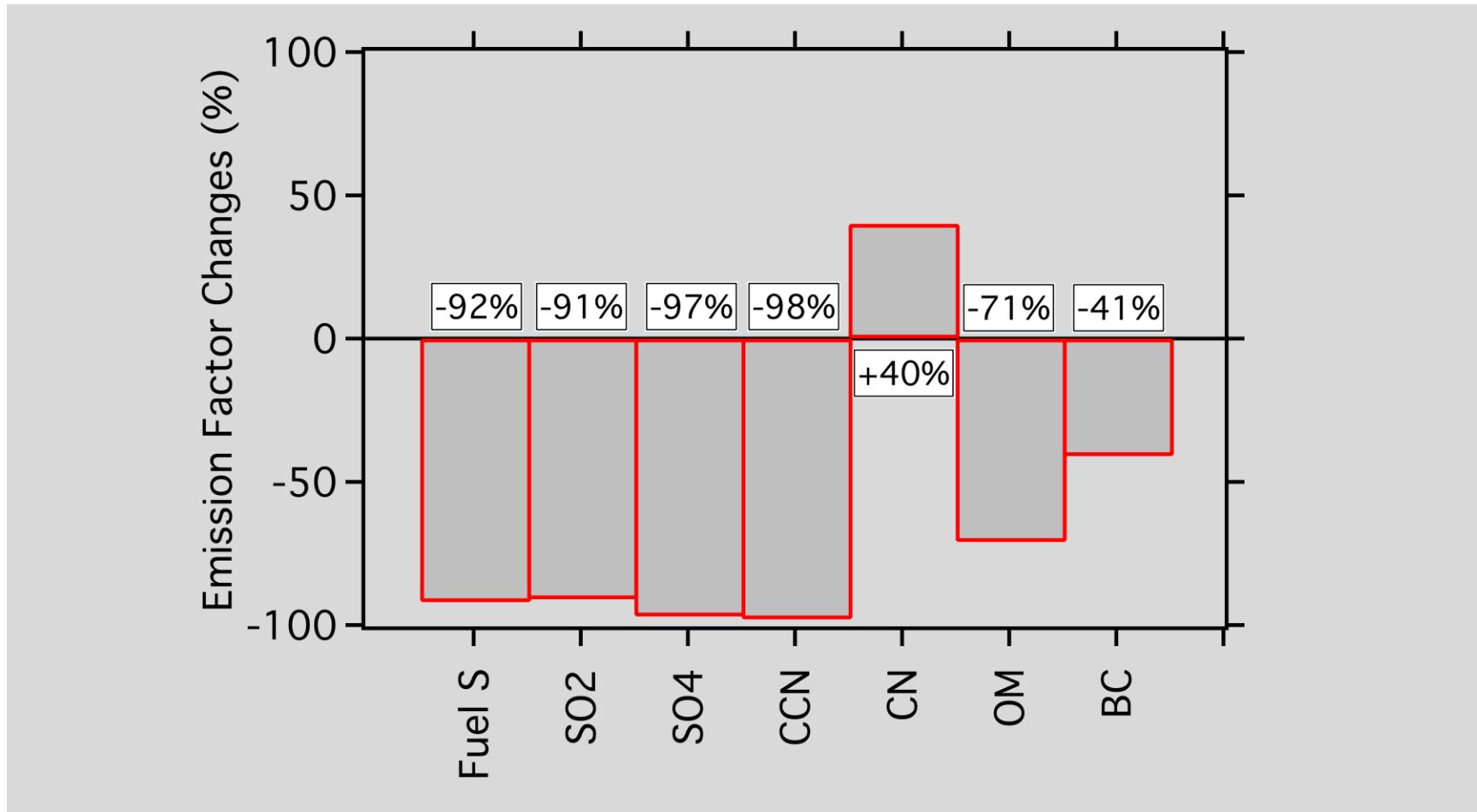




Emission Factors Across Fuel Switch



Δ Emission Factors Across Fuel Switch



N_2O source studies from the P-3: Quantify emissions from industrialized agriculture.

Bin Xiang et al., Harvard University

From NOAA:

Plane and NOAA
Payload

WRF Fields
(Wayne Angevine)

Land Use, Flight
Plans (Michael
Trainer)

From Harvard:

Flight N_2O sensor
(via NSF, NCAR)

Lagrangian Model
(STILT)

Detailed analysis
(*Bin Xiang and
her many helpers*)

N_2O emitted
 $= 3 \times \text{EDGAR}$

Question to Answer:

How can we improve the regional N₂O emission inventories for the state of California using CalNex observations?

Top-Down Method

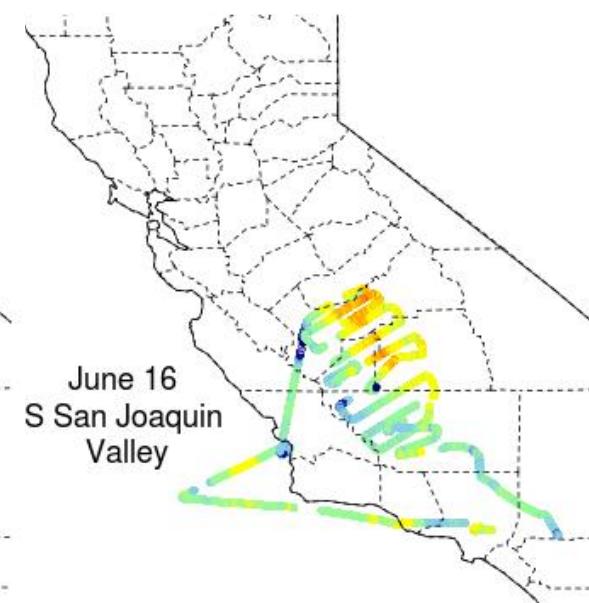
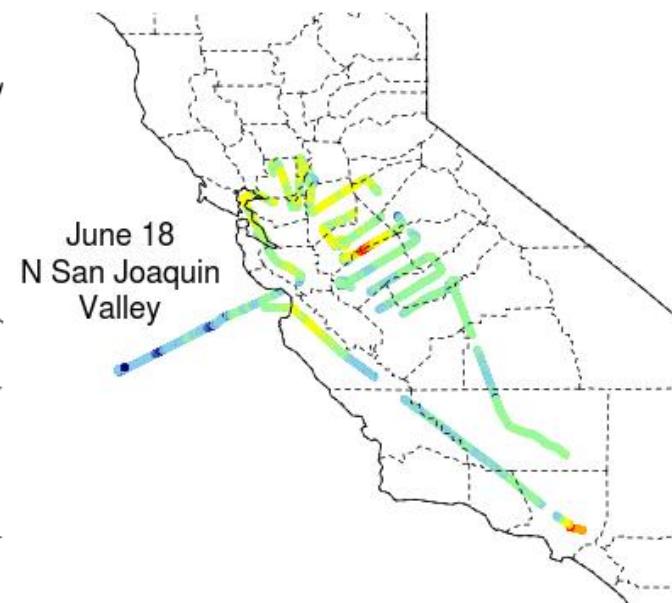
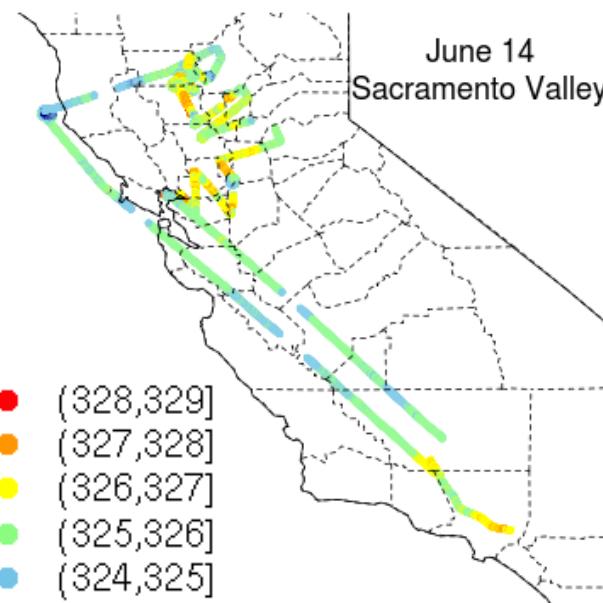
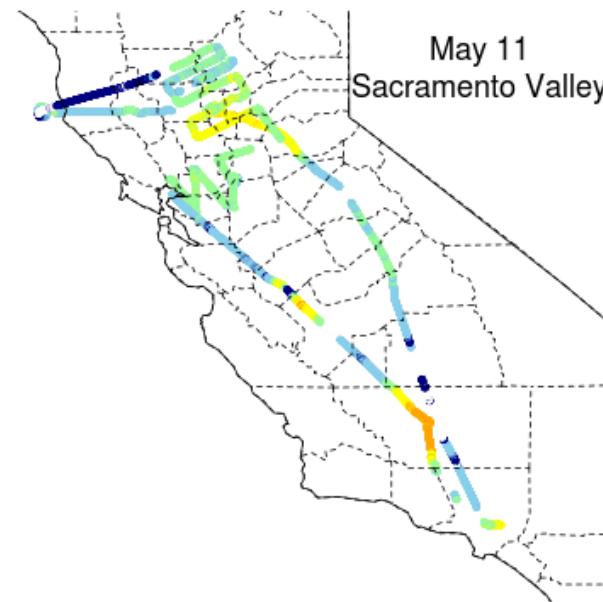
- ❖ **Transport model STILT** (Stochastic Time-Inverted Lagrangian Transport)
- ❖ **Meteorology** (WRF v3.2 provided by Wayne Angevine, NOAA)
- ❖ **Boundary condition** (HIPPO3 data [*NSF Program, March 2010*])
- ❖ **A priori input** (N₂O emission inventories, California land use maps)

$$\begin{aligned} N_2O_{simulated} &= N_2O_{boundary} + N_2O_{enhancement} \\ &= N_2O_{ocean} + N_2O_{remote_land} + N_2O_{local_land} \\ &= N_2O_{ocean} + N_2O_{remote_land} + (footprint \times surface_flux) \end{aligned}$$

Model-Data Assimilation

- ❖ Multiple linear regression

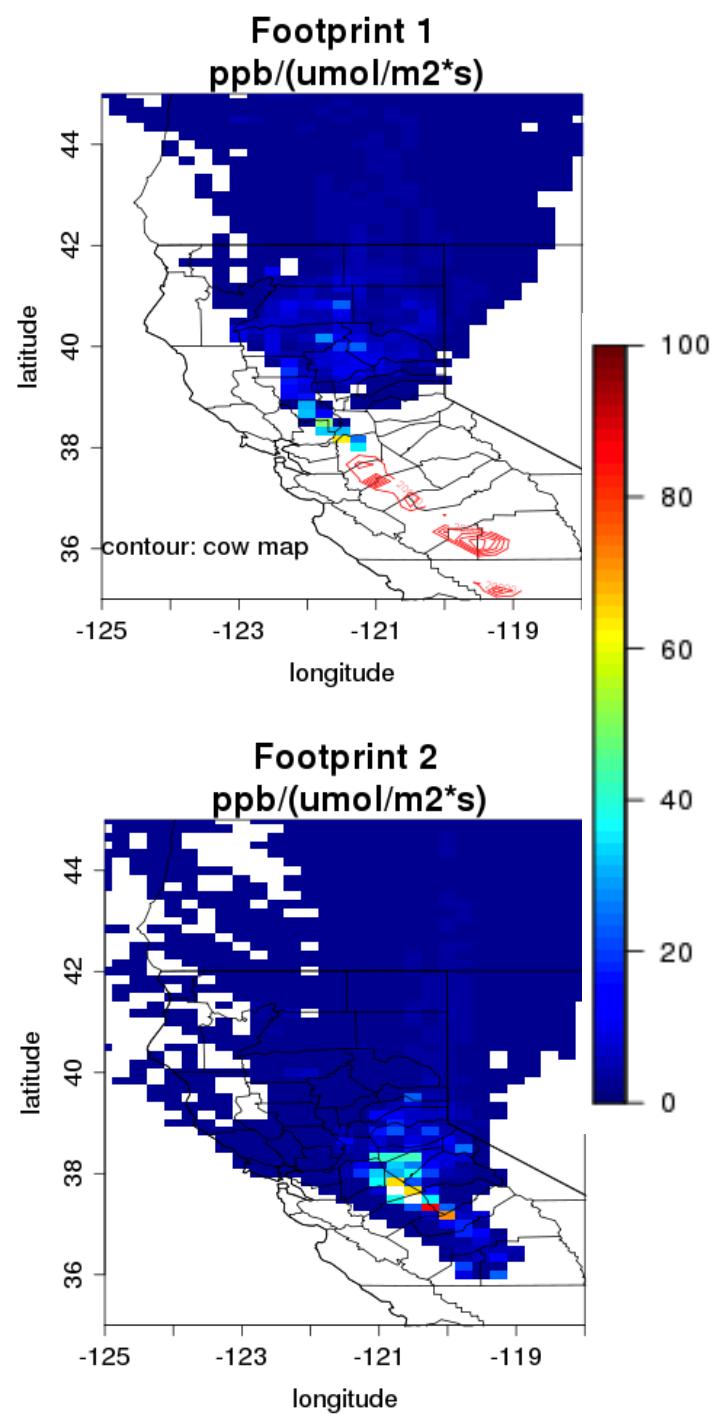
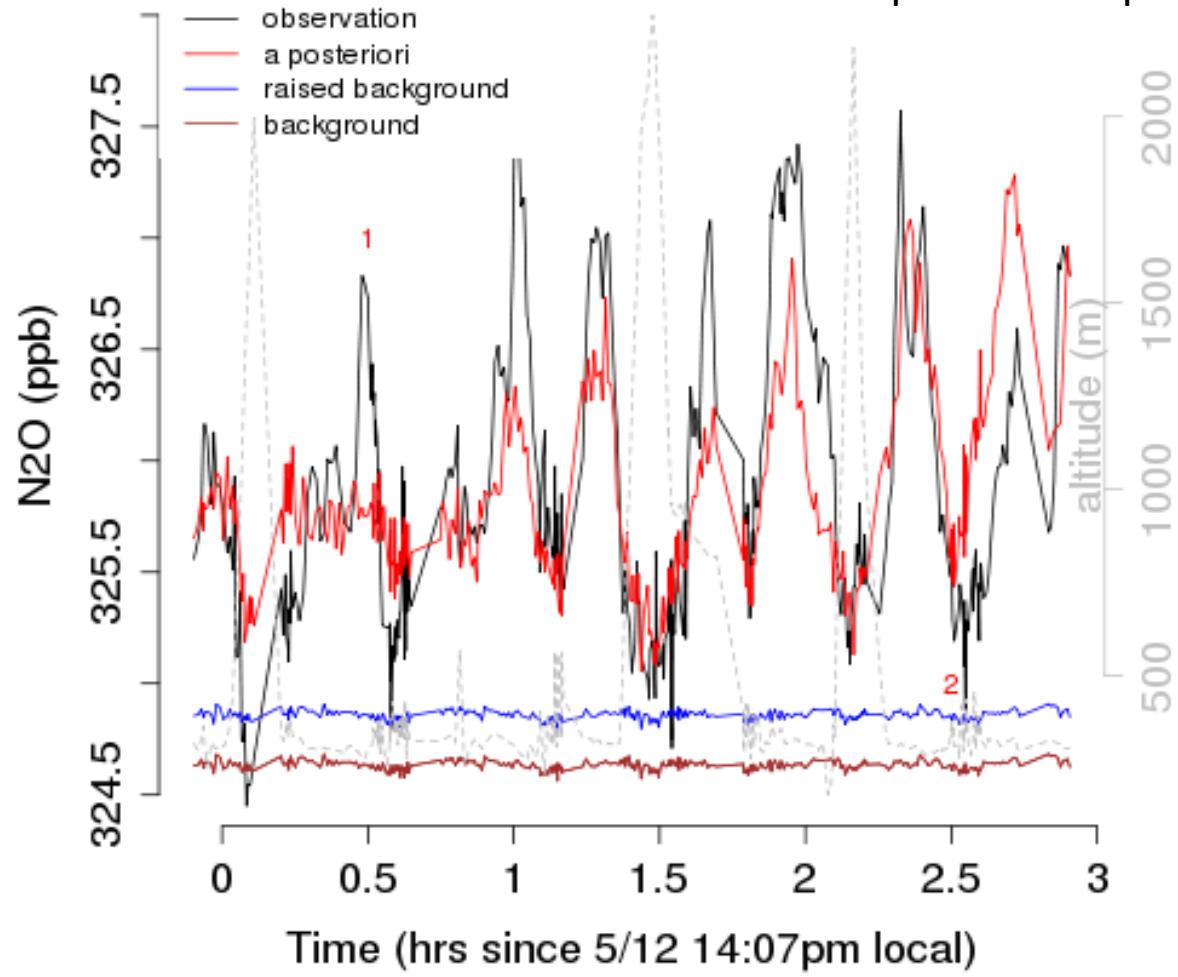
CalNex Agricultural N₂O Profiles



- (328,329]
- (327,328]
- (326,327]
- (325,326]
- (324,325]
- (323,324]

N₂O Linear Regression Results

California cow + crop + corn maps



Summary:

University contributions and collaborations in CalNex

Extremely diverse, leveraged, successful.

N₂O source studies:

Quantify emissions from industrialized agriculture.

Bin Xiang et al., Harvard University

From NOAA:

- the plane & payload
- Wayne Angevine's WRF fields
- Michael Trainer's land use data & flight planning, etc.

From Harvard (and NSF, NCAR):

- Lagrangian Particle Dispersion Model (STILT) to link concentrations to underlying sources
- Flight N₂O sensor (we built for NCAR, used on loan)

Result:

Emissions from corn, livestock, other crops \uparrow 3x (!)